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IGNITION STUDIES

PART V - STUDY OF THE PROCESSES OCCURRING DURING THE SPONTANEOUS IGNITION OF THE HEXANE ISOMERS

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PREVIOUS REPORTS IN THIS SERIES

"A Study of the Autoignition Properties of Certain Diesel
Fuels," J. E. Johnson, J. W. Crellin, and H. W. Carhart,
NRL Report 3859, Dec. 21, 1951

"Part II - The Spontaneous Ignition Properties of Some
Diesel Fuels and Pure Hydrocarbons," J. E. Johnson,
J. W. Crellin, and H. W. Carhart, NRL Report 4202,
July 20, 1953

"Part III - Ignition Properties of the Isomeric Hexanes,"
J. E. Johnson, J. W. Crellin, and H. W. Carhart, NRL
Report 4346, Apr. 30, 1954

"Part IV - Relation of Minimum Ignition Point to Other
Ignition Phenomena," J. W. Crellin, J. E. Johnson, and
H. W. Carhart, NRL Report 4476, Jan. 26, 1955

CONTENTS

ABSTRACT

Spontaneous ignition properties of the hexane isomers in air were studied using a uniformly heated one-liter spherical Pyrex flask. Particular emphasis was placed on pre-ignition reactions by means of measurements of internal gas temperature and oxygen consumption.

Time-temperature recordings of gas temperature were found to be helpful in distinguishing between ignition and non-ignition, but not between hot- and cool-flame ignition, although in most cases this distinction could be made visually in total darkness.

Minimum ignition temperature in air for cool- or hot-flame ignition, minimum reaction temperature, pre-ignition range, maximum temperature rise above base temperature, and oxygen consumption at ignition for the isomeric hexanes, appear to show correlation with ease of oxidation and ignition.

The present work suggests that minimum ignition temperature for cool- or hot-flame ignition may well be a more reliable criterion for fire safety than the commonly used SIT (hot-flame ignition only).

IGNITION STUDIES

PART V – STUDY OF THE PROCESSES OCCURRING DURING THE SPONTANEOUS IGNITION OF THE HEXANE ISOMERS

INTRODUCTION

Spontaneous Ignition

The spontaneous ignition properties of combustible materials, particularly fuels and hydrocarbons, have been an important area of combustion research for over fifty years. This interest in spontaneous ignition is based on the important role which this phenomenon plays in (a) the fire hazard in the handling and storage of combustibles, (b) the performance of various types of combustion engines, and (c) the elucidation of oxidation and combustion mechanisms of fuels, hydrocarbons, and related substances. Of these three phenomena, fire hazard and engine performance are of special importance to the Navy.

The spontaneous ignition temperature (SIT) of a substance is defined as that lowest temperature at which the substance will ignite in air without the aid of a spark or flame. Based on the thermal theory of ignition and on classical reaction-rate theory, spontaneous ignition temperature can be regarded as that temperature to which a combustible mixture must be raised so that the rate of heat evolved by the exothermic oxidation reactions of the system will just overbalance the rate at which heat is lost to the surroundings. The criterion that is usually taken to indicate ignition, however, is quite subjective. A commonly accepted definition of ignition is visible and/or audible combustion observed under ordinary laboratory conditions.

For reasons to be given later, it was found to be desirable in this work to modify this definition. Another complication is that, although the spontaneous ignition temperature of a substance should be a quantity related to some characteristic chemical property of the material, its experimentally determined value is markedly dependent on the method and apparatus employed for its determination. In a recent monograph, Mullins (1) reviews this subject including the importance, definition, and meaning of spontaneous ignition and spontaneous ignition temperature and describes numerous methods for its determination and the factors which influence results.

Earlier Studies

Earlier reports and publications from this Laboratory (2-6) describe ignition studies of diesel fuels and pure hydrocarbons utilizing a modified Jentzsch ignition tester (7). This apparatus is essentially an electrically heated combustion chamber coupled with an accurate oxygen-metering system in which ignitions and other fuel properties are determined at atmospheric pressure. This instrument, originally designed for fuel evaluation and testing by the German Navy, proved to be very versatile and useful for investigating spontaneous ignition properties.

The earlier NRL work covered the influence of oxygen concentration and temperature on ignition behavior. For each material investigated, curves were obtained which delineated three zones: (a) non-ignition, (b) cool-flame ignition, and (c) hot-flame ignition. A typical ignition curve is shown in Fig. 1.
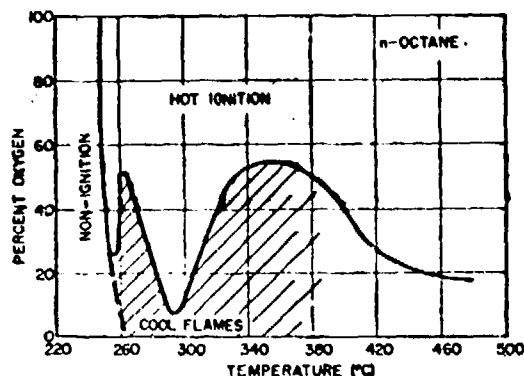
Fig. 1 - Ignition zones for a
typical hydrocarbon

Similar curves were obtained for a number of hydrocarbons and fuels, and these
curves are of particular interest regarding the relationship between spontaneous ignition
and fire hazard. Normally SIT is determined in air. Using n-octane (Fig. 1) as an exam-
ple, the SIT, or minimum temperature for hot ignition in air (21 percent oxygen), is about
280°C for the apparatus used. A slight change in apparatus, such as a larger chamber,
would cause the ignition curve to shift downward and to the left, so that the 21-percent
line would intersect the first lobe in the curve yielding a value which would be lower by
twenty degrees or more. In addition, at higher temperatures, "negative" ignition zones
are observed, since cool-flame ignition is observable only in total darkness, not usually
the condition in this type of determination. These factors introduce serious complications
in the proper interpretation of SIT as a fire-safety criterion.

These studies also included measurements of minimum ignition temperatures, ignition
delays, and apparent activation energies. The data were found to show a correlation
between molecular structure and ease of oxidation as well as other related oxidation and
ignition criteria such as octane number, cetane number, Hinshelwood's methyl retardation
factor, and relative oxidation rate.

Current NRL Study

Because of these interesting findings, it appeared fruitful to investigate certain of
these phenomena in more detail by use of more accurate instrumentation, with particular
emphasis on the pre-ignition reactions. The progress of these reactions was to be followed
by measurement of internal gas temperatures inside the combustion chamber by use of
a static rather than a gas flow system. The choice of a static system was made because
of its simplicity and the desire to make gas temperature-time measurements which would
not be feasible in a flow system. It was recognized that in this choice, an inherent fault of
a static method was the problem of uniform gas mixing after introduction of the hydro-
carbon sample. However, if the sample is discharged as a fine spray, rapid vaporization
and mixing with the air should occur, so that this problem will be minimized, particularly
in pre-ignition reactions which take relatively long compared to ignition reactions.

Despite the convenience and versatility of the Jentzsch tester, its geometry, its small
size, and other factors make it poorly suited for studying pre-ignition reactions and for
measuring gas-temperature data accurately. It was therefore decided to utilize a new

apparatus with a larger spherical chamber. The smaller surface-volume ratio would minimize surface effects and thus would aid in obtaining ignition temperatures less dependent on the apparatus used. Specifically, this apparatus would be used initially to study the spontaneous ignition processes of the isomeric hexanes and to correlate the findings with molecular structure.

APPARATUS

The apparatus* used by Setchkin (8) at the National Bureau of Standards for the determination of spontaneous ignition temperatures of combustible liquids was adopted for this work (Fig. 2). It consists of a one-liter spherical Pyrex flask inside a refractory casing. The surface-volume ratio of this flask is 0.56 cm^{-1} as compared to 2.0 cm^{-1} for the modified Jentzsch tester chamber, whose volume is approximately 22 cc. The neck, top, and bottom of the flask are each heated by separate heater coils controlled individually and manually by autotransformers. Temperature measurements are made by thermocouples located at each heater coil, the top and bottom of the flask, and one inside the flask, as shown. It was difficult to maintain uniform temperature control at predetermined temperatures by adjusting the autotransformers alone. Therefore a temperature controller was added which made it possible to maintain uniform temperatures within ±1°C.
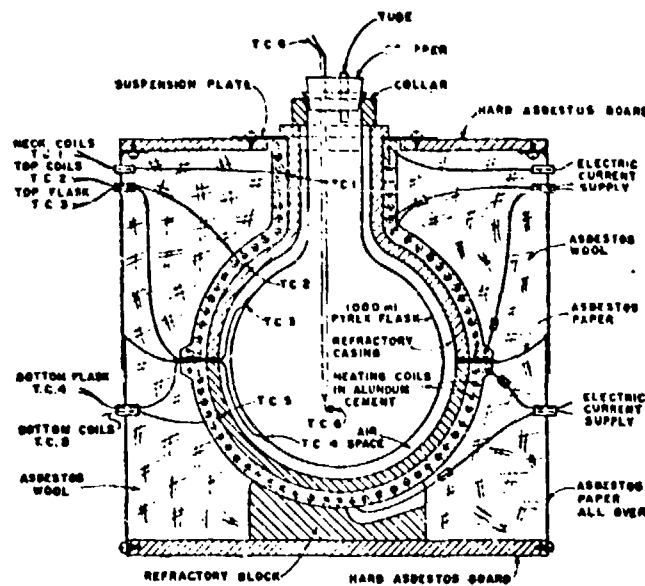

Fig. 2 - Ignition apparatus (from Setchkin, Ref. 8)

The important thermocouple in this system, T.C. 6, measures the temperature inside the flask. A fine chromel-alumel thermocouple (28 B and S gage) connected to a Weston Model 6701 fast-response recorder is used for this purpose. It was found necessary to use well-grounded shielding on the power cord, thermocouple leads, and the other wires

* Made by Research Appliance Co., Box 307, Allison Park, Pa.

leading into the recorder in order to eliminate external electrical interferences. All thermocouples were calibrated against a standard Pt/Pt-Rh thermocouple.

Setchkin investigated the effect of chamber size on the observed spontaneous ignition temperatures, testing flasks of the following sizes: 8 ml, 35 ml, 200 ml, 1 liter, 12 liters, and 15 liters. He reported a decrease in ignition temperatures with increase in chamber volume. Although slightly lower ignition temperatures were noted using the 12-liter and 15-liter flasks than with the 1-liter flask, he adapted the latter because the larger flasks were unwieldy and fragile.

Setchkin also looked into possible catalytic effects due to the exposed thermocouple inside the flask. Although he observed some effects of heat loss to the thermocouple, no catalytic effects were noted.

METHOD

After temperature adjustment had been made, the desired quantity, usually 0.2 ml, of hydrocarbon or fuel charge was injected into the flask by means of a hypodermic syringe fitted with a 6-inch, 26-gage needle, and stopwatch time was recorded. The lights were extinguished. Then the inside of the flask was observed in total darkness with the aid of a mirror supported over the flask stopper, while the temperature-time variations were being recorded. The time and type of ignition was noted, along with any other pertinent observations.

Thus far, all work has been done in air at atmospheric pressure, but plans have now been made to make ignition studies at other oxygen concentrations. The effect of variation in size of sample on ignition temperature is discussed by Setchkin (8), Frank et al.(9), and in the NRL work previously cited (3). In determining SIT by conventional methods, it is customary to try variation in sample size just below the ignition temperature to insure that the SIT repo 'ed will be the lowest temperature at which ignition will occur regardless of the concentration of the sample. Variation in sample size was also investigated in this work and is still under study. Thus far, it has been observed that, in certain instances, doubling the sample (0.4 ml) may result in cool flames instead of hot flames, and that decreasing the sample to about half or less at minimum ignition temperature may result in non-ignition. In all the work done thus far, small variations in sample size did not influence minimum ignition temperature values more than the experimental error of about 1°C, provided that no distinction was made between cool- and hot-flame ignition. Therefore, for uniformity, and to save time, a standard sample of 0.2 ml was used for the isomeric hexanes, since they have the same molecular weight, and very similar densities. This sample represents approximately 3.5 times the stoichiometric quantity assuming complete oxidation in air at 300°C.

In the initial stages of this investigation, a fresh clean flask was used for each run. It was observed, especially at temperatures close to the spontaneous ignition temperature, that erratic and nonreproducible results were obtained. By "conditioning" a flask with repeated use, this difficulty was overcome. The same flask therefore was used throughout.

In order to obtain additional information regarding the processes of ignition being studied, gas samples were taken for oxygen analysis after the reactions were completed. The oxygen concentration immediately after the charge was vaporized, but prior to oxidation, was calculated from the perfect gas law. Oxygen determinations were made after ignition by means of a Pauling magnetic susceptibility oxygen meter on 100-ml samples obtained from inside the flask with a large hypodermic syringe fitted with a fine tube. After the gas sample was taken for oxygen determination, the gases in the flask were blown out with compressed air for about two minutes. Then, after temperature adjustment, the apparatus was ready for the next run.

The hydrocarbons studied were Phillips Petroleum Company 99 mol percent purity and each was purified further by percolation through silica gel and alumina.

TYPES OF IGNITION OBSERVATIONS

At least four different types of observations were noted (Table 1), depending on the fuel and on the base temperature. Typical temperature-time ignition curves superimposed in a single diagram are illustrated for 2,3-dimethylbutane (Fig. 3). In the figure exact magnitudes and positions are not intended to be necessarily significant as these curves have been sketched in for illustrative purposes only. The initial dip in each curve is caused by cooling due to vaporization of the sample. Curve 1 is negative; curves 2-9 are pre-ignition, non-luminous reactions; curve 10 represents a cool-flame ignition and curve 11, a hot-flame ignition. Although in this example the hot flame shows a greater temperature increase than that of the cool flame, this was not always found to be the case, owing to inertia of thermocouple response.

Table 1
Types of Ignition Observations

Classification	Observation (Visible and/or Audible as Seen in Total Darkness)	Temperature Rise
Negative	None	None
Pre-ignition, Non-luminous reactions	None	Gradual
Cool-flame ignition	Faint silent bluish glow*	Sudden
Hot-flame ignition	Ranged from faint silent yellowish glow* to flames of varying colors (yellow, orange, blue), and varying intensity and audibility (from weak "pop" to intense explosion), often accompanied by smoke of varying amounts, sometimes sufficient to mask substantial flames unless observed in total darkness	Sudden

*Visible only in total darkness

Certain generalizations can be made concerning these observations. Hot- or cool-flame ignition could be detected by means of a sudden temperature rise, or peak on the temperature-time curve and, in most cases, could be detected visually in total darkness. Pre-ignition reactions were detectable only by means of the temperature-time trace. Cool-flame ignition was distinguishable from hot by visual observation. Cool flames and certain hot flames could not be observed except in total darkness, but they were always detectable by means of the temperature-time traces.
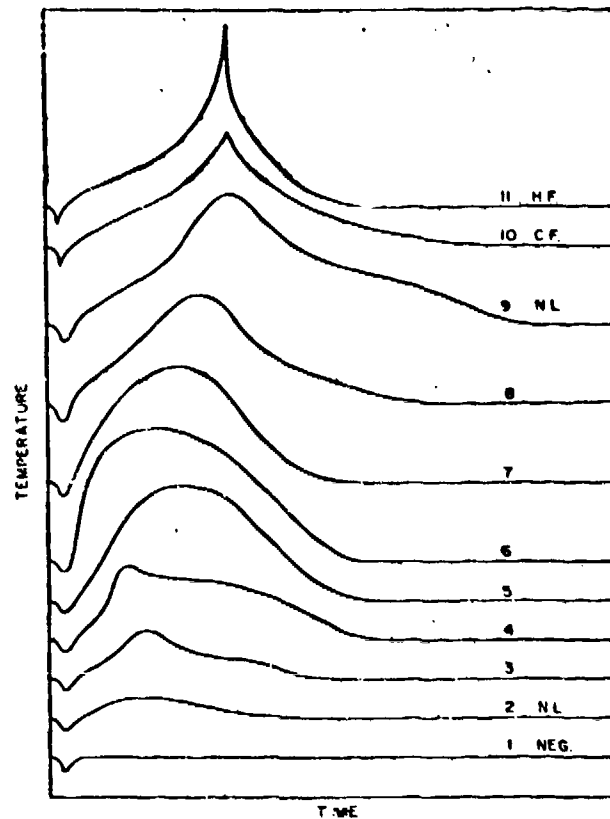
Fig. 3 - Typical ignition curves for
2,3-dimethylbutane in air (curves sketched
in for illustrative purposes only)

In the present study, rather than attempt to distinguish between the minimum hot-flame ignition temperature (SIT) and cool-flame ignition temperature, it was decided to accept either cool flame or hot flame as representing positive ignition.

RESULTS

Pre-ignition curves for the isomeric hexanes showing temperature rise and oxygen consumption versus base temperature are shown in Figs. 4-6. The term "base temperature," as used in this report, refers to the initial temperature of the flask just prior to introducing the fuel sample. This term is referred to frequently as "block temperature" or "initial temperature" in combustion literature.
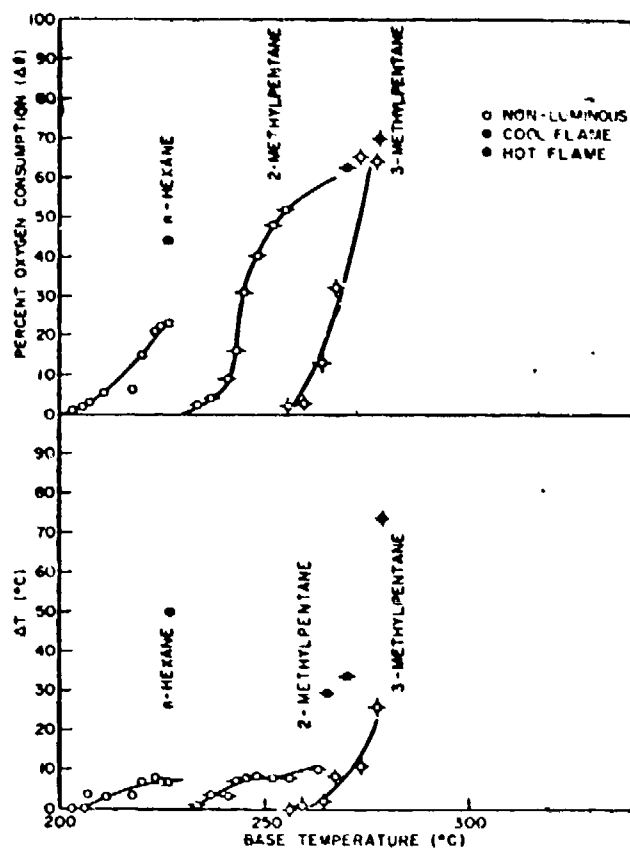
Fig. 4 - Temperature rise and oxygen consumption
versus base temperature in pre-ignition zones for
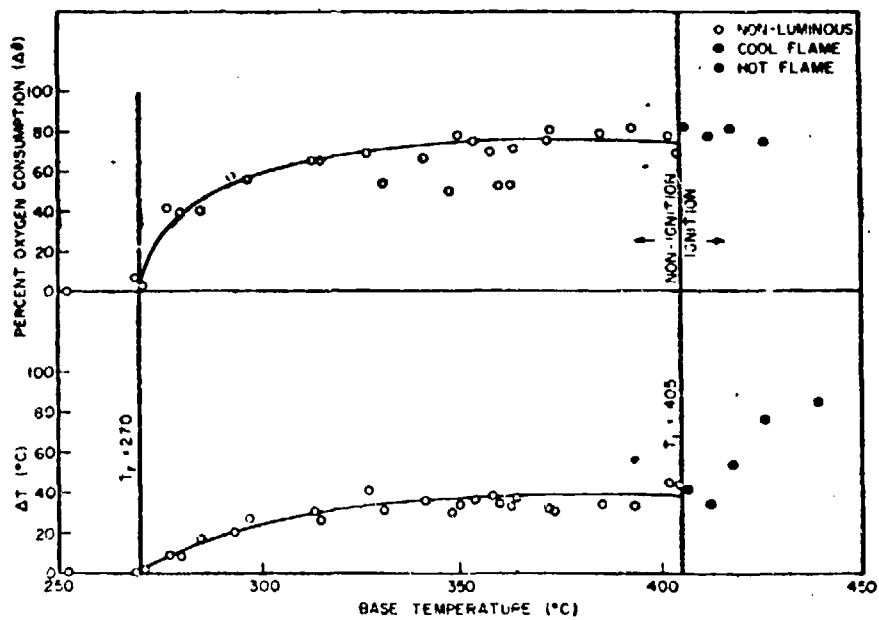hydrocarbons in air

Fig. 5 - Temperature rise and oxygen consumption versus base
temperature in pre-ignition zones for 2,2-dimethylbutane in air
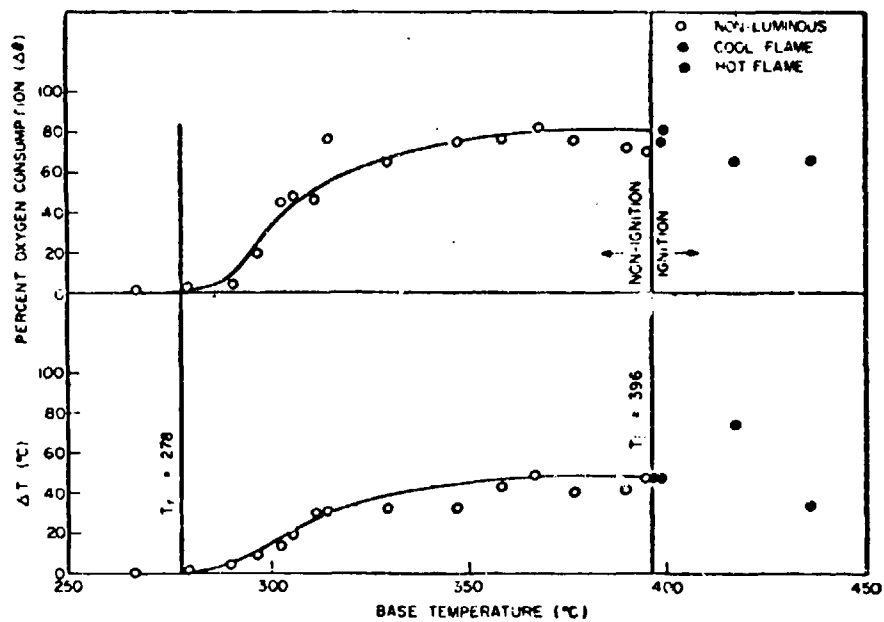
Fig. 6 - Temperature rise and oxygen consumption versus base
temperature in pre-ignition zones for 2,3-dimethylbutane in air

Data are summarized in Table 2, where:

T_r is the minimum reaction temperature, or the lowest base temperature at which a measurable temperature rise ΔT is observed. In general T_r also corresponds to the lowest temperature at which the measurable oxygen consumption $\Delta\theta$ is noted.

T_i is the minimum base temperature for cool- or hot-flame ignition.

$(T_i - T_r)$ is the pre-ignition, or non-luminous reaction zone. Relative positions and magnitudes of these zones are shown in Fig. 7.

ΔT is the temperature rise above the base temperature.

$\Delta\theta$ is the oxygen consumption.

$\Delta\theta_s$ and ΔT_s represent the values obtained by extrapolation to T_i of a plot of $\Delta\theta$ and maximum ΔT values respectively versus base temperature in the pre-ignition zone. Examples of these plots are shown in Figs. 4-6.

Table 2
Summary of Pre-ignition Data

Hexane Isomer	T_r (°C)	T_i (°C)	$T_i - T_r$ (°C)	ΔT_s (°C)	$\Delta\theta_s$ (%)
n-Hexane	206	227	21	9	23
2-Methylpentane	233	264	31	11	52
3-Methylpentane	259	278	19	27	65
2,2-Dimethylbutane	270	405	135	38	74
2.3-Dimethylbutane	278	396	118	50	82

DISCUSSION

Although the data obtained thus far are preliminary, it is of interest to examine them and make a few tentative observations which will guide future experiments in this work.

The isomers listed in Table 2 are in the usually accepted order of increasing resistance to oxidation, and appear to fall into two groups. In general, the more easily oxidized group including n-hexane and the two methylpentanes have lower T_r and T_i values, and much shorter pre-ignition ranges $(T_i - T_r)$ than the two dimethylbutanes which are more difficult to oxidize. The data more or less follow this same order within the two groups (see Figs. 4-7).

It was of interest to compare T_r and ΔT_s with the relative oxidation rates (ROR) obtained by Cullis and Hinshelwood (10). These ROR values were derived from oxidation rate data and the comparison is shown in Figs. 8 and 9. They were calculated by these workers from temperature-corrected reaction-velocity constants relative to unity for 2,3-dimethylbutane. The linearity of the curves suggests a correlation between ROR and T_r, and ΔT_s. In Fig. 9, only n-hexane is off the line. It would be expected that ROR might show closer relation to T_r than to T_i, since it was determined under more similar experimental conditions, i.e., below ignition temperature.
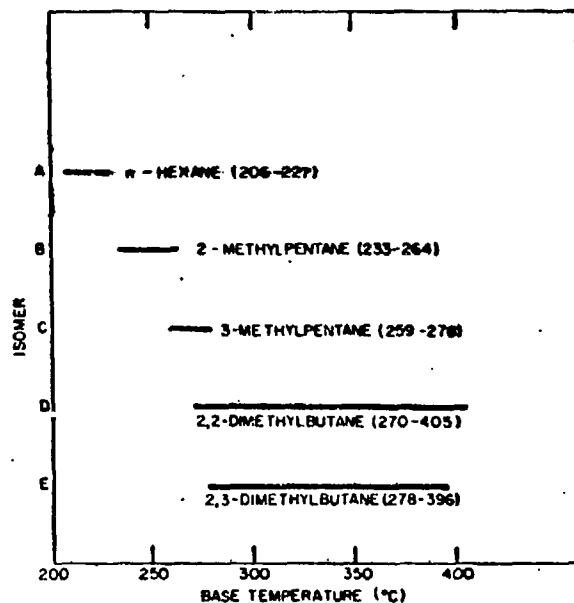
Fig. 7 - Pre-ignition temperature ranges
(minimum reaction temperature to ignition
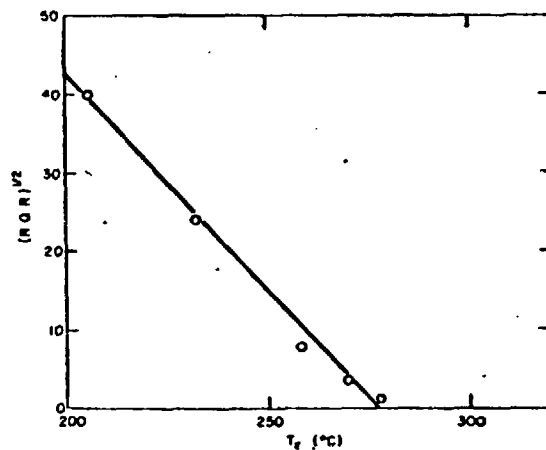temperature) for isomeric hexanes in air

Fig. 8 - Comparison of relative oxidation rate
(Cullis and Hinshelwood) with minimum reaction
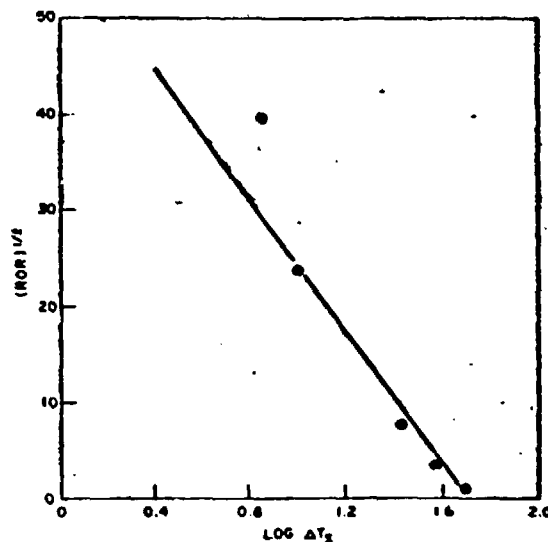temperature for isomeric hexanes in air

Fig. 9 - Comparison of relative oxidation rate
(Cullis and Hinshelwood) with ΔT_s for isomeric
hexanes in air

Correlation is also shown in Fig. 10 between T_r (this work) and minimum ignition
point (MIP) values from the earlier NRL work (5), where MIP is the lowest temperature
of either cool- or hot-flame ignition in an atmosphere of fuel plus 100 percent oxygen.
In this curve, the 2,3-dimethylbutane is the only isomer which does not fall directly on
the line.

It was pointed out in the introduction that conventional SIT determinations leave much
to be desired because such values may be seriously in error due to differences in environ-
mental conditions such as size of ignition chamber, oxygen partial pressure, etc. Such
changes, it was stated, may cause shifts in ignition curves, so that at a given base temper-
ature in a particular apparatus cool flames might occur rather than hot flames. The cool
flame, being ephemeral in character, is not observed ordinarily and this could lead to
improper data which could produce a false sense of security. Any sudden temperature
rise, even when due to a cool flame, represents a rapidly accelerating oxidation reaction
which in a different and especially a larger enclosure could lead to a fire or explosion.
From the point of view of fire safety it would therefore appear desirable to have ignition
determinations conducted in total darkness with the aid of gas temperature measurements,
and as has been shown in this work, that T_i (cool or hot flame) be used as a criterion for
fire safety.

SUMMARY

1. Earlier ignition studies at NRL have been extended using a larger apparatus and
more refined instrumentation. Special emphasis was placed on the study of pre-ignition
reactions by means of measurements of internal gas temperatures and oxygen consumption.
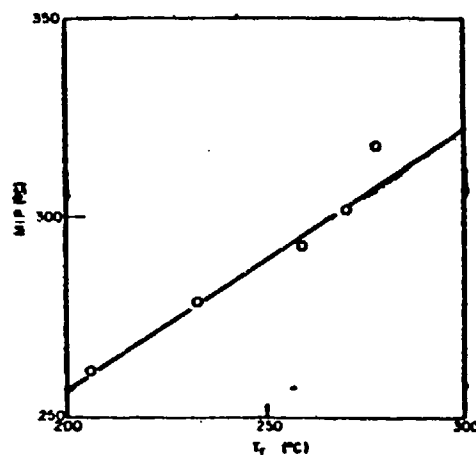
Fig. 10 - Comparison of minimum ignition
point (Johnson, Crellin, and Carhart) with
minimum reaction temperatures for the
isomeric hexanes in air

2. In addition to minimum ignition temperature in air for cool- or hot-flame ignition,
four other quantities were suggested as tools in ignition studies: minimum reaction
temperature, pre-ignition range, temperature rise, and oxygen consumption at ignition.
From the data obtained thus far, there appears to be a correlation between these values
and the ease of oxidation and ignition.

3. For safety purposes, the minimum ignition temperature in air might well be
more reliable for cool- or hot-flame ignition than the conventional SIT, as it is not as
dependent on oxygen concentration or atmospheric pressure. It might be best to deter-
mine SIT in total darkness, and it is suggested that temperature-time measurements of
the internal gas temperature be used as guidance in establishing criteria for ignition.

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